

# ACETYLENE-MEDIATED ALKYLATION OF MONOALKYL CARBONATES AND CARBAMIC ACIDS WITH *TERT*-AMINE

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Carbonic acid diesters and carbamic acid esters are useful organic substances as intermediates for the syntheses of pharmaceutical, agricultural, and the other chemicals. They are currently synthesized in industry using the processes based on phosgene or carbon monoxide. On the other hand, since carbon dioxide is an abundant and cheap carbonyl carbon source, and is much less toxic than those raw materials, substantial efforts have been focused on its fixation into carbonyl compounds including carbonic acid diesters and carbamic acid esters.<sup>1</sup> However, their syntheses based on carbon dioxide reported so far require rather expensive substrates like alkyl halides, and are not competitive with the currently adopted industrial processes.

The author and his co-workers previously reported that carbamic acids derived from CO<sub>2</sub> and *sec*-amines reacts with alkynes to give vinyl *N,N*-dialkylcarbamates in the presence of Ru complexes.<sup>2</sup> However, a similar reaction using alcohols, which would give vinyl alkyl carbonates, failed probably because of the insufficient nucleophilicity of alcohols compared with *sec*-amines,<sup>3</sup> save that acetylenic alcohols react with CO<sub>2</sub> to give cyclic carbonates, 2-oxo-propyl alkyl carbonates, 2-oxo-propyl *N,N*-dialkyl-carbamates, or 4-methyl-2-oxo-1,3-oxazolines in the presence of *tert*-amine, *sec*-amine, or *prim*-amine respectively.<sup>4</sup> During the attempt of reacting monoalkyl carbonates with acetylene in the presence of *tert*-amine and Ru complexes, however, a slight formation of dialkyl carbonates was observed. Further investigation revealed that this product is formed even in the absence of ruthenium or any other transition metal complexes. This means that this reaction is totally different from the ruthenium catalyzed synthesis of vinyl *N,N*-dialkyl carbamates. Moreover, one of the alkyl groups of dialkyl carbonates was found to come from *tert*-amines originally added with the intention of increasing the nucleophilicity of alcohols while the other from alcohols. Thus, either symmetric or unsymmetric carbonic acid diesters are formed as a main product according to the alkyl groups of alcohols and *tert*-amines[eq. (1)].



Also formed are alkyl *N,N*-dialkylcarbamates, all the alkyl groups of which are originated from *tert*-amines. Therefore, this reaction may be represented as the alkylation of monoalkyl carbonates and carbamic acids with *tert*-amines; carbamic acids are considered to be formed from CO<sub>2</sub> and *sec*-amines resulting from the dealkylation of *tert*-amines.

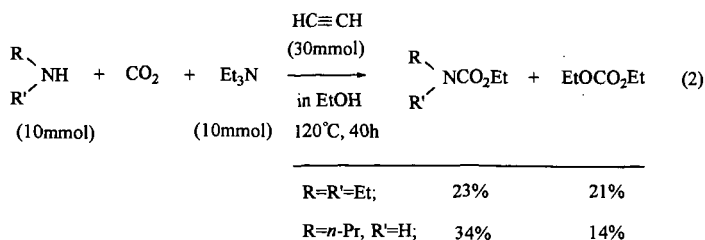
In a typical experiment, acetylene(30mmol) is introduced in a 50mL-autoclave containing *tert*-amine(30mmol) and alcohol(200mmol) at -50°C. After CO<sub>2</sub> is pressurized at 5MPa at ambient temperature, the autoclave is heated at a designated temperature for 16h or 40h. The products obtained are identified by spectroscopical comparison with their authentic samples either purchased or synthesized using chloroformic acid esters and analyzed by GLC. Unreacted *tert*-amines and acetylene recovered together with CO<sub>2</sub> through an accumulated gas-flow meter are also analyzed by GLC.

In the reaction with ethanol and triethylamine, diethyl carbonate and ethyl *N,N*-diethylcarbamate are

formed in fair yields at the reaction temperatures higher than 120°C, while practically no product is obtained at 80°C as shown in Table 1. The conversion of acetylene increases significantly with reaction temperature, while that of triethylamine levels out at about 42% with the result that the total yield of diethyl carbonate and ethyl *N, N*-diethylcarbamate based on triethylamine remains at 40% even at 180°C; but, the selectivity for these products is as high as 95%. Triethylamine is recovered unreacted in the reaction without acetylene even at 160°C. On the other hand, acetylene is mostly consumed and 33% of triethylamine is converted in the reaction without CO<sub>2</sub>, but naturally there is no CO<sub>2</sub> containing product formed. This means that the presence of CO<sub>2</sub> rather suppresses the conversion of acetylene to some extent.

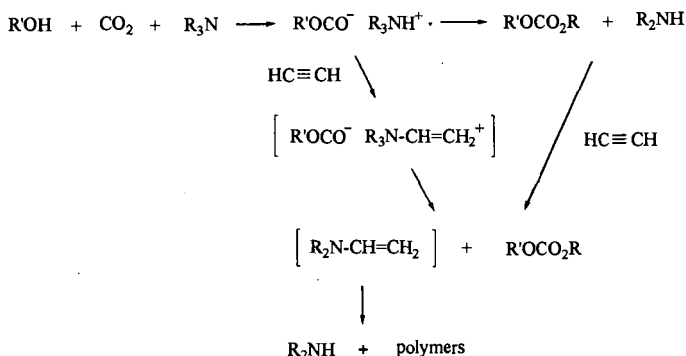
The yield of diethyl carbonate and the conversion of triethylamine increase from 32% and 45% to 78% and 83% respectively with decrease in the amount of triethylamine introduced from 30mmol to 5mmol in the reaction at 160°C for 40h as shown in Table 2. The yield of ethyl *N, N*-diethylcarbamate, on the other hand, reaches its maximum at 13% with 20mmol of triethylamine(entry 2). Neither diethyl carbonate nor ethyl *N, N*-diethylcarbamate is formed without triethylamine(entry 5). When triethylamine is used in smaller amounts, a significant formation of diethylamine is observed in the resulting reaction solution, which accounts for the formation of ethyl *N, N*-diethylcarbamate; *N, N*-diethylcarbamic acid derived from CO<sub>2</sub> and diethylamine formed by the preceeding alkylation of monoalkyl carbonate must be alkylated in place of monoalkyl carbonate with triethylamine. It is also found that diethylamine is partially converted to triethylamine and small amounts of diethyl carbonate and ethyl *N, N*-diethylcarbamate are formed in the reaction using diethylamine instead of triethylamine(entry 6). These results, as well as the fact that the total yield(86%) of the products exceeds the conversion of triethylamine(83%) in the reaction with 5mmol of triethylamine(entry 4), suggest that more than one ethyl group in triethylamine can be used for alkylation but most probably at the expense of higher consumption in acetylene under certain conditions.

The results of the reactions with several alcohols and *tert*-amines are summarized in Table 3. When *n*-propanol is used instead of ethanol, ethyl *n*-propyl carbonate is formed in the yield of 22% together with ethyl *N, N*-diethylcarbamate(7%) and di-*n*-propyl carbonate(1%). This result clearly shows that one of the ethyl group of diethyl carbonate formed in the reaction with ethanol mostly comes from triethylamine. The slight formation of di-*n*-propyl carbonate, however, suggests that the ester exchange reaction of dialkyl carbonate occurs to some extent in excess alcohols. This reaction becomes rather significant when allyl alcohol is used probably because of its high nucleophilicity; 19% of ethyl allyl carbonate is formed together with diallyl carbonate(8%) and ethyl *N, N*-diethylcarbamate(14%). It is not yet clear why the carbamate is obtained in such a high yield in this reaction compared with the other saturated alcohols. Tri-*n*-propylamine can be also used in place of triethylamine for the reactions of these alcohols, although it shows a little lower reactivity; 12-21% yields of the corresponding *n*-propyl carbonates are formed together with small amounts of symmetric carbonates and *n*-propyl *N, N*-di-*n*-propylcarbamate. All the reaction solutions are homogeneous but colored in brown when the reaction has proceeded, while the use of either methanol or trimethylamine results in the formation of polymers probably because of their excessive reactivity toward acetylene.



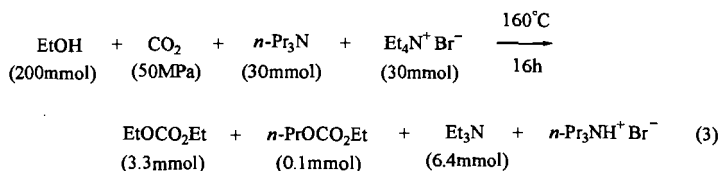
The effect of the addition of *sec*- or *prim*-amine is demonstrated in eq. 2. When diethylamine is added to the reaction of ethanol and triethylamine at 120°C for 40h, ethyl *N,N*-diethylcarbamate is formed in a higher yield(23%) than diethyl carbonate(21%). On the other hand, the addition of *n*-propylamine leads to the formation of ethyl *N,n*-propylcarbamate in good yield(34%); also formed are less amounts of diethyl carbonate(14%) and *N,N*-diethylcarbamate(5%).

There are two possible mechanisms for the present reaction as shown in Scheme 1; one includes the nucleophilic attack of monoalkylcarbonate,  $\text{ROCO}_2^-$ , on to one of the three alkyl radicals of hydrotrialkylammonium,  $\text{R}_3\text{NH}^+$ , followed by the addition of the liberated *sec*-amine to acetylene so that the equilibrium should be shifted to the right by giving dialkylvinylamine,  $\text{R}_2\text{N-CH=CH}_2$ , and the other includes the attack of monoalkylcarbonate on to trialkylvinylammonium,  $\text{R}_3\text{N-CH=CH}_2^+$ , formed by the preliminary addition of hydrotrialkylammonium to acetylene. In either case, although dialkylvinylamine itself has not yet been detected by GLC analysis probably because of its instability under the reaction conditions, its temporal formation seems plausible, because acetylene is substantially consumed during the reactions and converted to some polymeric materials, which can be observed after distilling the reaction solutions. Therefore, it is considered that dialkylvinylamine is partially decomposed to dialkylamine and acetylene polymers, and partially polymerized as such.



Scheme 1 Estimated reaction mechanism.

The following experiment has been performed in order to obtain a deeper understanding about the reaction mechanism. When the reaction of ethanol,  $\text{CO}_2$ , tri-*n*-propylamine, and tetraethylammonium bromide is performed under similar conditions as described in Table 1, diethyl carbonate is obtained in the yield of 3.3mmol while only a small amount(0.1mmol) of ethyl *n*-carbonate is formed(eq. 3).



This result indicates that the monoethyl carbonate formed from ethanol and  $\text{CO}_2$  does not react with its counter cation, hydro-tri-*n*-propylammonium, but with tetraethylammonium added, thereby suggesting that the latter mechanism including the preliminary formation of trialkylvinylammonium is likely. This process is analogous to the insertion of hydrotrialkylammonium hydroxide<sup>5</sup> or

chloride<sup>6</sup> to acetylene giving trialkylvinylammonium salt,  $R_3N-CH=CH_2^+ X^-$ . The following step, the attack of monoalkylcarbonate to trialkylvinylammonium giving dialkyl carbonate, is analogous to the esterification of carboxylic acids with large steric hindrances by forming tetramethylammonium salts and their thermal decomposition.<sup>7</sup>

The present reaction not only provides a new synthetic method of carbonic and carbamic acid esters involving only industrially available starting materials, but also shows a new type of  $CO_2$  fixation without catalyst.

#### References

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Table 1. Effect of the Reaction Temperature<sup>a)</sup>

No.	Temp. (°C)	— Yield(%) <sup>b)</sup> —		— Conv.(%) —	
		EtOCO <sub>2</sub> Et	Et <sub>2</sub> NCO <sub>2</sub> Et	Et <sub>3</sub> N	HC≡CH
1	180	32	8	42	85
2	160	30	9	41	74
3	140	28	9	39	66
4	120	19	5	28	44
5	100	4	0	10	34
6	80	0	0	6	18
7 <sup>c)</sup>	160	0	0	3	-
8 <sup>d)</sup>	160	0	0	33	97

<sup>a)</sup>  $CO_2$ (5MPa),  $Et_3N$ (30mmol),  $EtOH$ (200mmol), Acetylene(30mmol), 16h.

<sup>b)</sup> based on triethylamine. <sup>c)</sup> without acetylene. <sup>d)</sup>  $Ar$ (5MPa).

Table 2. Effect of the Amount of Et<sub>3</sub>N<sup>a)</sup>

No.	Et <sub>3</sub> N (mmol)	— Yield(%) <sup>b)</sup> —		— Conv.(%) —	
		EtOCO <sub>2</sub> Et	Et <sub>2</sub> NCO <sub>2</sub> Et	Et <sub>3</sub> N	HC≡CH
1	30	32	11	45	96
2	20	42	13	56	86
3	10	65	12	77	80
4	5	78	8	83	83
5	0	-	-	-	21
6 <sup>c)</sup>	0	4	1	- 9	81

<sup>a)</sup>CO<sub>2</sub>(5MPa), EtOH(200mmol), Acetylene(30mmol), 160°C, 40h.<sup>b)</sup>based on amine. <sup>c)</sup>Et<sub>2</sub>NH(5mmol).Table 3. Effect of the Alcohols and *tert*-Amines<sup>a)</sup>

R <sub>3</sub> N	R'OH	— yield(%) <sup>b)</sup> —			— conv.(%) —	
		R'OCO <sub>2</sub> R	R'OCO <sub>2</sub> R'	R <sub>2</sub> NCO <sub>2</sub> R	R <sub>3</sub> N	HC≡CH
Et <sub>3</sub> N	EtOH	30	-	9	41	74
Et <sub>3</sub> N	<i>n</i> -PrOH	22	1	7	35	68
Et <sub>3</sub> N	CH <sub>2</sub> =CHCH <sub>2</sub> OH	19	8	14	42	89
<i>n</i> -Pr <sub>3</sub> N	EtOH	17	3	2	26	46
<i>n</i> -Pr <sub>3</sub> N	<i>n</i> -PrOH	12	-	1	16	38
<i>n</i> -Pr <sub>3</sub> N	CH <sub>2</sub> =CHCH <sub>2</sub> OH	21	6	4	32	56

<sup>a)</sup>R<sub>3</sub>N(ca. 30mmol), R'OH(200mmol), acetylene(30mmol), CO<sub>2</sub>(5MPa), 160°C, 16h,<sup>b)</sup>based on amine.